RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 19 15 NOVEMBER 1992-I

First-principles study of He in Si

M. Alatalo
University of Helsinki, Research Institute for Theoretical Physics, Siltavuorenpenger 20 C, 00170 Helsinki, Finland and Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

M. J. Puska and R. M. Nieminen
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland
(Received 9 July 1992)

We have performed first-principles calculations for He atoms in a Si lattice. From dynamic total-energy minimization we obtain the relaxations of the Si atoms around the impurity and the corresponding total energies. The calculated heat of solution and the diffusion constant of He in Si are in good agreement with experiment. There is a net attraction between two tetrahedral He interstitials, leading to a binding energy of 0.08 eV for He atoms at neighboring interstices. On the other hand, Si vacancies are found not to trap He atoms. The consequences of these results to He-bubble nucleation and growth are discussed.

Noble-gas impurities in semiconductors are of great interest for several reasons. The existence of noble-gas atoms in a semiconductor, often due to the fabrication techniques or irradiation damage, can change the electrical properties of the material, which makes the study of their effects important from a technological point of view. Also, the use of helium in spectroscopic techniques[1,2] requires understanding of the behavior of He in semiconductors. On the other hand, there is much fundamental interest concerning, e.g., the interactions of noble-gas atoms with the host semiconductor and the diffusion processes. Yet there are very few theoretical or experimental[3–5] studies of these systems, especially on the microscopic level.

In this paper we report *ab initio* molecular dynamics calculations for He in Si. The solution energies needed to implant the He atom in both tetrahedral and hexagonal interstitial sites are examined as well as the relaxations of the Si lattice around the He atom. Moreover, we study the interaction between *two* tetrahedral He interstitials. We also discuss the interaction between a He atom and a silicon vacancy. From these results one can deduce information on the He migration paths and the question of He bubble nucleation and growth.

In the present calculation we use the first-principles molecular-dynamics scheme proposed by Car and Parrinello.[6] A simple cubic 64-atom supercell is used. Norm-conserving pseudopotentials constructed using the method of Bachelet, Hamann, and Schlüter[7] are used for both Si and He. We use the s nonlocality only, the nonlocal part of the pseudopotential being treated by the Kleinmann-Bylander procedure.[8] The Ceperley-Alder exchange-correlation functional[9] is used in the form parametrized by Perdew and Zunger.[10] The energy cutoff for the plane-wave expansion is set to 8 Ry, which corresponds to about 1500 plane waves per eigenstate. Only the Γ point is used for the Brillouin-zone sampling. With these parameters we obtain the equilibrium lattice constant $a = 10.0a_0$ for bulk Si, which is slightly smaller than the experimental value of $a = 10.26a_0$. The time step in the dynamic simulations is 5.5 a.u. ($= 1.7\times10^{-16}$ s) and the consistent value of the electronic mass parameter $\mu = 400$ a.u. The atomic masses are changed between different calculations which is justified because their values only affect the time scale of the calculation but not the total energy.

We first consider a He atom embedded at different interstitial (tetrahedral and hexagonal) sites in bulk Si. These sites are shown schematically in Fig. 1. First the electronic structure of the system is calculated using the steepest-descent method for the electronic degrees of freedom only. When the electronic structure corresponding to the minimum total energy is found, we let the Si atoms move according to their equations of motion.[6] To obtain the potential-energy surface for the impurity the He atom is fixed to its position by giving it a much larger mass (up to 1000 amu) than for the Si atoms.

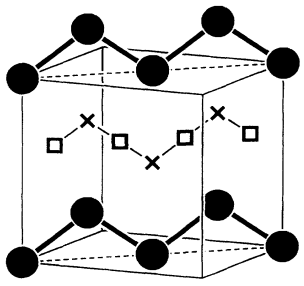

FIG. 1. A schematic presentation of the [110] plane of Si. Closed circles denote Si atoms, the tetrahedral sites are marked by crosses, and the hexagonal sites by squares. The He migration path is a zigzag line through the interstitial sites.

TABLE I. Nearest-neighbor breathing mode relaxations Δd_{NN}, relaxation energies E_{rel}, and heats of solution ΔH of a He atom in tetrahedral and hexagonal interstitial site in silicon. The heats of solution are given for two different plane-wave cutoff energies E_c. The heat of solution in the tetrahedral site near vacancy [Fig. 3(b)] is also given. Finally, the heats of solution for a second He in the supercell are shown in the cases where the first He is at a bulk tetrahedral site and at the tetrahedral site near the Si vacancy.

	Δd_{NN} (%)	E_{rel} (eV)	ΔH (eV) E_c = 8 Ry	ΔH (eV) E_c = 11.8 Ry
Tetrahedral site	1.7	−0.06	0.88	0.77
Hexagonal site	4.4	−0.27	1.97	1.59
He + tetrahedral site	1.1	−0.17	0.80	
Vacancy			1.03	
He + vacancy			0.94	

The relaxations of the Si atoms next to the He interstitials are shown in Table I. In both cases the relaxations are of pure breathing type and their direction is outwards, reflecting the repulsive interaction between the closed-shell He and the host Si electron states. The small amplitude of the relaxation results in a small energy gained by letting the atoms move away from their positions in the ideal lattice. The relaxation is smallest when He is situated in the tetrahedral site where the distance to the surrounding Si atoms is largest. In this case the next-nearest-neighbor relaxations are fairly small (less than 1%) and the effects arising from the finite size of the supercell can thus be expected to have a negligible contribution to the results.

The heats of solution ΔH are obtained from the total-energy calculations as follows:

$$\Delta H = E_{\mathrm{Si+He}} - E_{\mathrm{bulk}} - E_{\mathrm{He}}, \quad (1)$$

where $E_{\mathrm{Si+He}}$ is the total energy for the 64-atom Si supercell with a He at the interstitial site, E_{bulk} is the total energy for the pure 64-atom Si supercell, and E_{He} is the total energy of a He atom. To check the reliability of our calculations we have performed the calculations for ΔH associated with the different interstitial sites with two different cutoff energies, the larger being E_c=11.8 Ry. Our results are shown in Table I. The experimental heat of solution for He in Si (Ref. 4) is 0.48 eV, which is smaller than our lower value of 0.77 eV at the tetrahedral site. The accuracy of the old permeation experiments of Ref. 4 may, however, not be good enough for a strict comparision. The difference in the solution energies between the tetrahedral and hexagonal sites is, according to our calculation, 0.82 eV. As discussed below, this difference is the main contribution to the diffusion activation energy.

It is interesting to compare the energetics of He in Si with the so-called effective medium theory (EMT), developed originally for describing the impurity-metal interactions.[12] According to EMT the main contribution to the solution energy of an impurity atom into the host electron system is a function of the unperturbed electron density at the nucleus of the impurity atom. In the case of He, this function depends in practice linearly on the electron density with the constant of proportionality $\bar{\alpha}_{\mathrm{eff}} = 250\ \mathrm{eV}a_0^3$.[13] The linear rise reflects the repulsive interaction with the electron gas. It results from the increase in kinetic energy when more and more host electron states have to be orthogonal to the bound 1s state of He. Therefore, He prefers regions of low electron density. Although the EMT is originally formulated for impurity atoms in metals, it has been shown to describe well also the interactions between rare-gas atoms.[14] Therefore, we expect it to give a reasonable description for He in Si. The electron density is higher at the hexagonal site than at the tetrahedral site, the difference being $\Delta n = 0.0028a_0^{-3}$. This density difference is calculated with the Car-Parrinello method following the EMT idea, i.e., without He present but using the lattice relaxations induced by the impurity. The proportionality constant $\bar{\alpha}_{\mathrm{eff}}$ predicts an energy difference of 0.7 eV, which is in good agreement with the difference between the tetrahedral and hexagonal site energies given in Table I.

We have also performed a simulation in which the He atom is set to the hexagonal interstitial site with its physical mass. When we allow the atoms to move, the He atom first stays practically at its initial position for 500 time steps (= 6.6×10^{-14} s) and then starts to move in the [111] direction towards the tetrahedral site. After another 400 time steps it reaches the tetrahedral site where it remains oscillating with an attenuating amplitude. This is illustrated in Fig. 2. The average frequency of this oscillation is ω = 20 THz which is an estimate for the frequency of the local mode for a He atom at

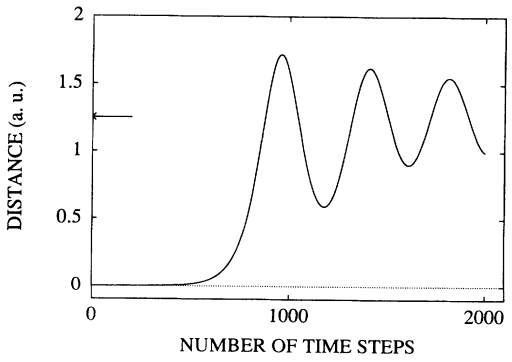

FIG. 2. The time evolution of the position of the He atom along the [111] direction. The distance is measured from the hexagonal site. The arrow indicates the position of the tetrahedral site.

the tetrahedral site. The highest total energy recorded during the movement of He from the hexagonal to the tetrahedral site is only 0.02 eV larger than that in the hexagonal site. Therefore, using the heats of solution calculated with the 11.8-Ry cutoff, we can deduce that the migration barrier E_m along the interstitial channels (see Fig. 1) is 0.84 eV. This value is within the limits of 0.58 and 1.26 eV for the diffusion activation energy, quoted in Ref. 11.

The migration energy and the frequency of oscillations can be used in estimating the diffusion coefficient for He in Si. First, the frequency of 20 THz corresponds to the quantum-mechanical zero-point energy of ~0.04 eV for He in the tetrahedral site. This is an order of magnitude smaller than the migration energy, so that we can use the classical picture for He diffusion. If the vibrational entropy contributions are not taken into account the diffusion coefficient for classical hopping along the interstitial channels has the form[11]

$$D = d^2 \omega e^{-E_m/k_B T}. \quad (2)$$

Above, d is the distance along the zigzag-shaped channels between two tetrahedral sites, i.e., $d = 3.06a_0$. Using the calculated values for the migration barrier and the oscillation frequency we get an estimate for the diffusion coefficient which is in good qualitative agreement with experiment:[4] For the temperature of 1471 K we obtain the value $D = 7 \times 10^{-5}$ cm^2/s, while the experimental value of van Wieringen and Warmoltz[4] is 6×10^{-5} cm^2/s. Unfortunately, the measurements span only a narrow temperature range and therefore a reliable comparison between the theoretical and experimental temperature dependence of the diffusion coefficient is not possible.

In order to study the early stages of He bubble formation in Si (Ref. 15) we have performed calculations with *two* He atoms in the simulation cell. The first He atom is set to a tetrahedral site and the second He is brought to the tetrahedral site next to the first one. From this calculation we obtain the solution energy for the second He which is 0.08 eV lower than that for a single He atom (Table I). This value can be regarded as the binding energy of the He atom pair in Si. In the fcc metal Ni the corresponding energy is 0.2 eV.[21] The lower value of the binding energy in a semiconductor can be explained by the more open lattice structure. Therefore, as discussed above, the lattice relaxation is small and the energy gain associated with the relaxation of the atoms around the second He is smaller than in metals.

We have also studied the He-Si vacancy interaction. In Fig. 3 we show schematically the atomic geometries associated with a Si vacancy and a vacancy-interstitial He pair. The clean vacancy is in the neutral charge state so that two electrons occupy the deep levels in the band gap.[16] The vacancy has a tetragonal symmetry, in which the four Si atoms around the empty site form two pairs. Within the pairs the distances of the atoms are smaller than the distance between atoms in different pairs. Compared to the unrelaxed, ideal vacancy, each of the Si atoms neighboring the vacancy has moved towards the center of the vacancy by 18.5% (breathing component of the relaxation) and then, in order to make pairs, perpendicular to this direction by 13.6% (pairing component of the relaxation) of the perfect lattice bond distance. This kind of inward relaxation is in agreement with several recent first-principles calculations.[17–20] The He atom is situated originally at the center of the Si vacancy. When the optimal electronic structure for this configuration is found and the atoms are allowed to move, the He atom starts to move in the [100] direction and ends up in the neighboring tetrahedral site between two unpaired Si atoms. The He atom causes its nearest neighbors to relax outwards, which distorts the tetragonal symmetry of the nearest neighbors of the clean vacancy.

The movement of the He atom from the center of the vacancy to the interstitial tetrahedral site can again be understood using EMT arguments. Namely, the electron density is *higher* at the center of the vacancy than at the interstitial regions. This is due to the dangling bonds. Actually, the solution energy of the He atom into the tetrahedral site next to the vacancy site is 0.15 eV *larger* than the solution energy to the tetrahedral site in the bulk lattice. This is because the inwards relaxation of the Si atoms neighboring the vacancy decreases the open volume and increases the electron density at the tetra-

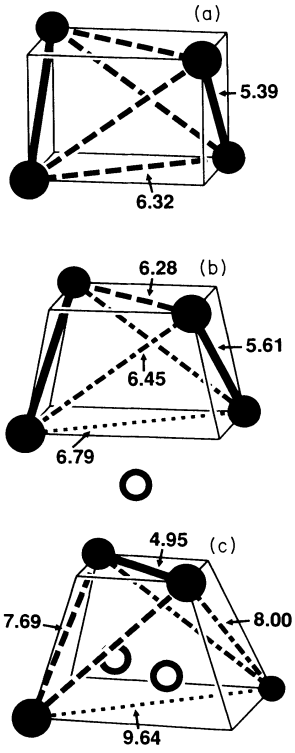

FIG. 3. The structure of (a) a clean neutral vacancy in Si, (b) a He-vacancy pair, (c) a complex of two He and a vacancy. The four nearest Si atoms of the vacancy (at the center of the cage) are denoted by closed circles and the He atoms by open circles. The equivalent distances (in Bohr radii) between Si atoms are shown by similar lines, i.e., solid, dashed, dash-dotted, and dotted lines in order of increasing distance.

hedral site next to the vacancy. Thus, a single vacancy does not act as a trapping center for He atoms.

Finally, we have studied what happens when a second He atom is added to the vacancy-He pair. The two He atoms occupy now distorted tetrahedral sites adjacent to the center of the vacancy. This is shown schematically in Fig. 3(c). As given in Table I the solution energy of the second He to the vacancy is 0.09 eV lower than that of the first He. This is slightly surprising because the lattice relaxations associated with this defect are large. However, the solution energy still remains higher than that at the bulk tetrahedral site, confirming the conclusion that the vacancy does not act as a trapping center.

Our results indicate that the growth of the He bubbles can begin by clustering of interstitial He, as in the model by Wilson, Bisson, and Baskes for He in metals.[21] Unfortunately, the present type of calculations, with a finite supercell size limited by computer resources, cannot be used for the simulation of the later stages of the bubble growth. Therefore, it remains unresolved if the interstitial He cluster can analogously to the model by Wilson, Bisson, and Baskes[21] collapse at some critical size so that a He bubble and interstitial Si atoms are produced. The energy gain due to the decrease of the He solution energy in the collapse should be larger than the energy associated with the creation of vacancies and interstitials. We have calculated the vacancy and interstitial formation energies for Si to be 1.8 and 4.7 eV, respectively. These energies may, however, be considerably reduced in the vicinity of the He cluster.[21]

In conclusion, we have performed first-principles molecular-dynamics calculations for He in Si showing the tendency of He to the tetrahdedral interstitial sites. The calculated solution energy of He in Si is 0.77 eV, which is in good qualitative agreement with experiment. The He atoms at the neighboring tetrahedral sites are shown to bind together with the binding energy of 0.08 eV. We have also shown that a vacancy in Si cannot act as a nucleation center for He atoms.

The authors wish to thank Dr. K. Laasonen for many useful discussions. We acknowledge the generous computing resources obtained through Center for Scientific Computing, Espoo, Finland.

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